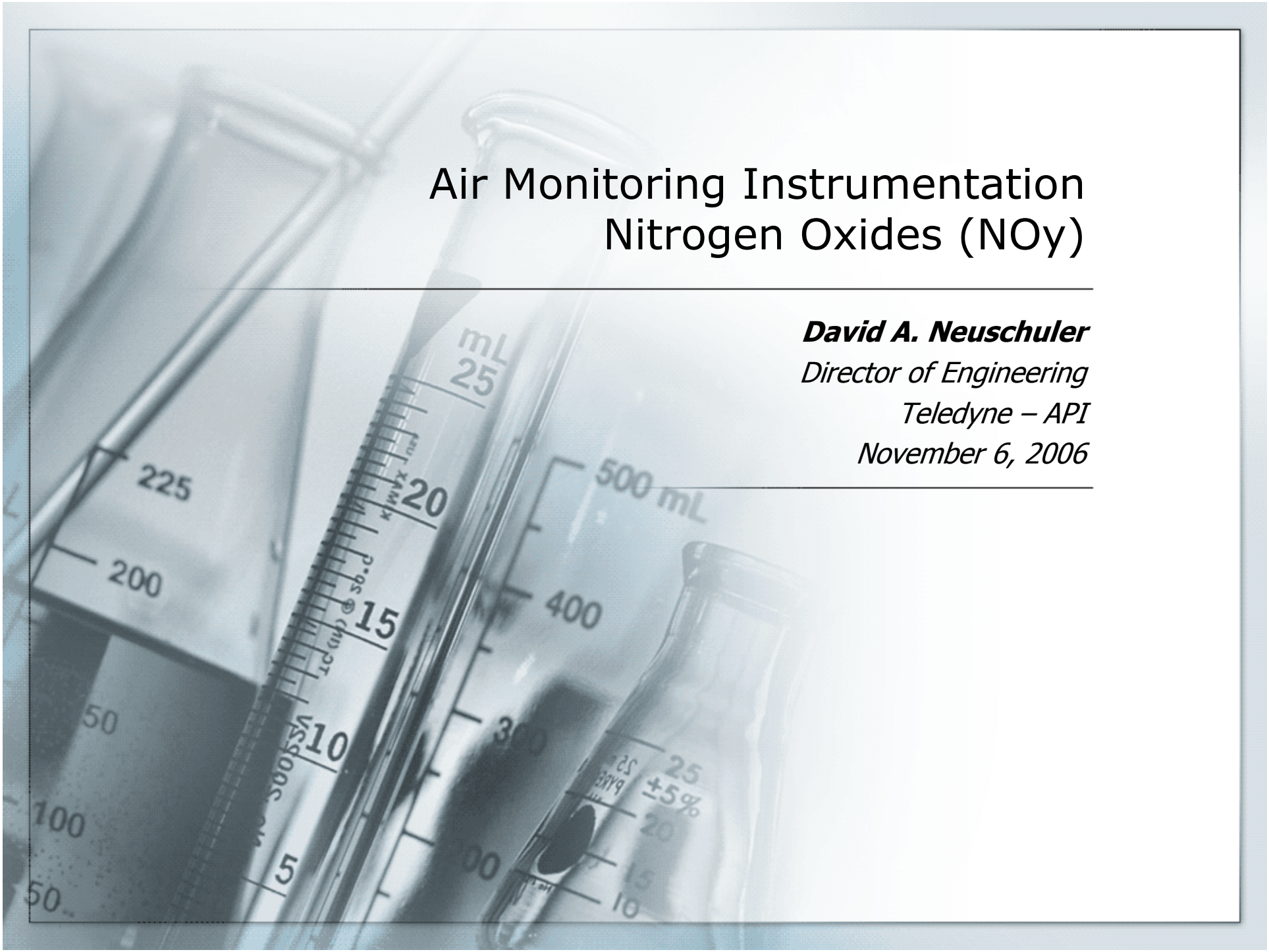

# Air Monitoring Instrumentation
# Nitrogen Oxides (NOy)


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*November 6, 2006*

# What is NOy

- Total Reactive Nitrogen

  "Collective name for oxidized forms of nitrogen in the atmosphere such as nitric oxide (NO), nitrogen dioxide ($NO_2$), nitric acid ($HNO_3$), and organic nitrates; usually designated by $NO_y$." - *AMS*

- Precursors in the formation of Ozone
- Definitions

  NOy = NOz + NOx

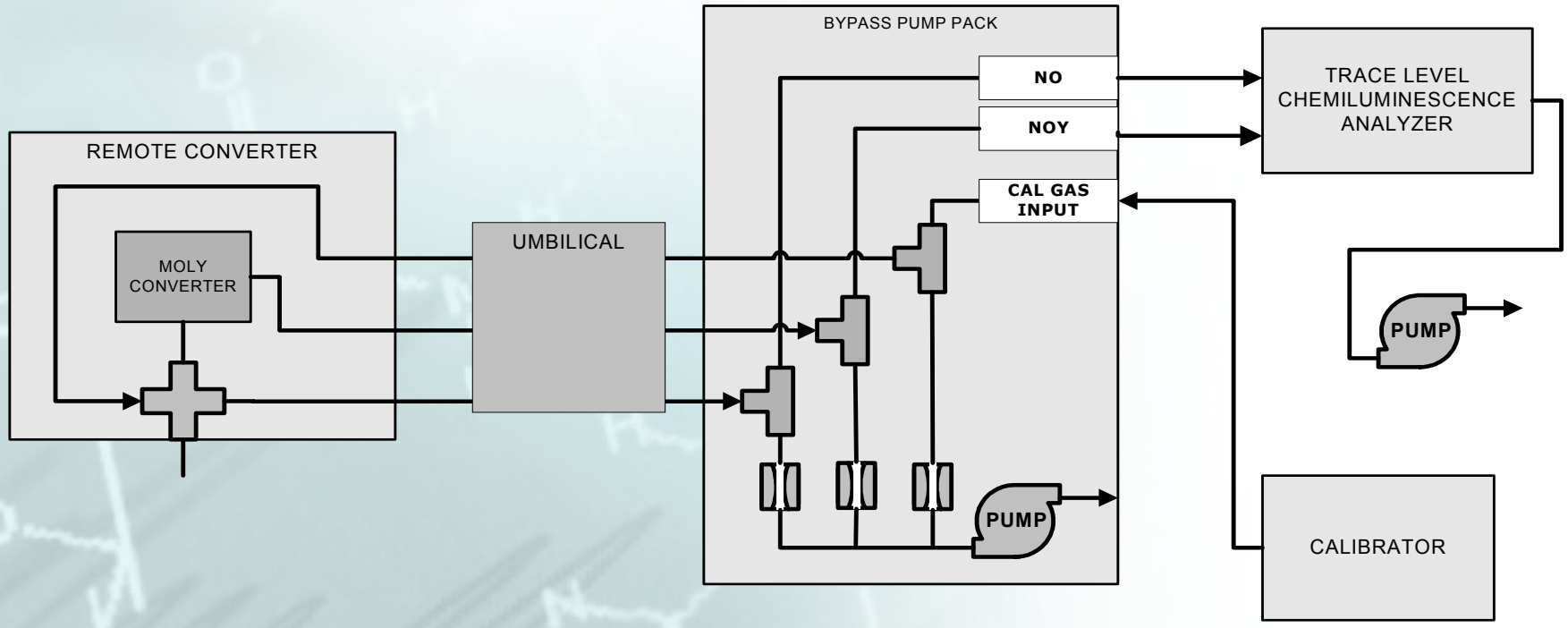
  NOx = NO + NO2

  NOz = $HNO_3$ + HONO + $2N_2O_5$ + $HO_2NO_2$
  + PAN + $NO_3$ + Organic Nitrates – but **not** $NH_3$
- Some NOz compounds have short lifetimes
- $NO_2$ specific analyzer required to measure NOz

# Technique

- Measurement using Nitric Oxide-Ozone Chemilumescence analyzer
- Conversion of NOy species to NO
  - Molybdenum ~325°C
  - Gold with CO or H2 injection ~ 400°C
  - Vitreous Carbon ~ 350°C
  - Ferrous Sulfate
- Converter as near inlet as possible with no sample filter
- Requires trace level analyzer for useful measurement
- Minimizing residence time essential to good measurement

# Simple Pneumatic Block Diagram



# Analyzer Differences

| Specification or Characteristic | Standard NOx Analyzer | Premium NOx Analyzer | Purpose |
|---|---|---|---|
| LDL | <400 ppt | <50 ppt | |
| zero drift 24 hours | <500 ppt | <100 ppt | |
| zero drift 7 days | <1000 ppt | <200 ppt | |
| Propylene reject. Ratio | | >20,000:1 | |
| Ethylene reject. Ratio | | >40,000:1 | |
| | | | |
| | | | |
| PMT Anode Sensitivity | 2500 A/lm | 3000 A/lm | More sensitivity, higher SNR |
| Reaction Cell | Non-plated | Gold Plated | Increased signal out |
| Flow Rate | 500 ccm | 1000 ccm | Increased signal out |
| Nominal Cell Pressure | 5" HgA | 2.5" HgA | Increased sensitivity |
| Autoref scheme | Autozero stop sample flow | Autozero with prereactor | Improved hydrocarbon rejection |

# Inlet Materials

(or how can we keep **"It"** from sticking)

- "**It**" = gasses that readily stick to surfaces especially nitric acid and ammonia
- **Causes** memory effect leading to excessive rise and fall times:
  - Operation – over or under actual value, smear features
  - Calibration – Elevated zeros, reduced spans
- Exacerbated by long tubing, low temperatures

# Inlet Materials

Standard**:** ¼" stainless tubing, adapters and fittings

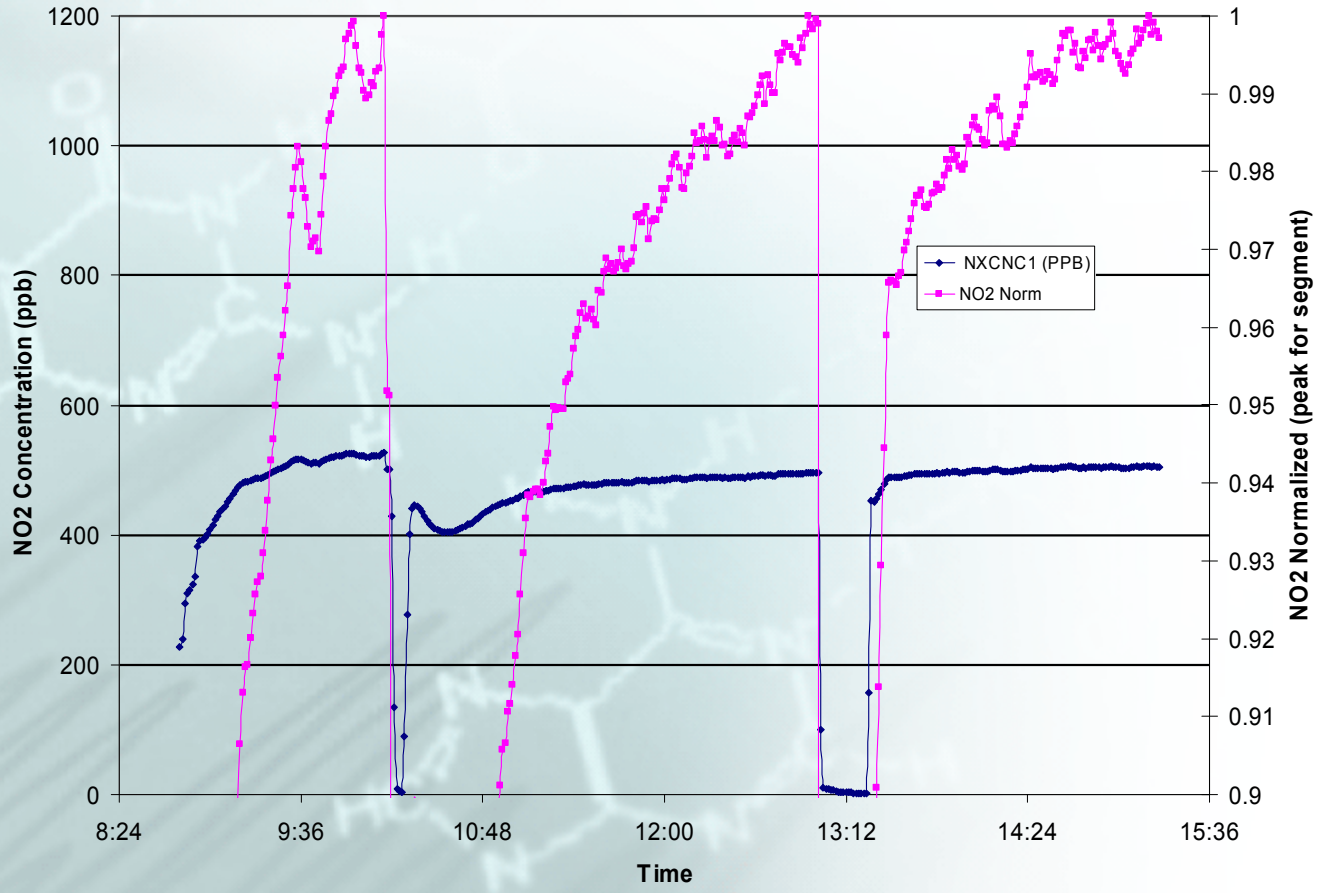
Field Testing:

- SilcoSteel® (hydrogenated amorphous silicon) coated, stainless for inlet and other NOy wetted surfaces, including body and inlet tubing of converter
- PFA bulkhead, cross and tubing to within ½" of converter inlet; converter inlet and body SilcoSteel® coated

# Calibration

- Gases: Nitric, iPan, nPan, $NO_2$, NO/GPT
  - No SRM
  - Nitric: very difficult to use
  - N-propyl nitrate: difficult to obtain & questionable analog for nitric
  - Iso-propyl nitrate: readily available
- Errors in verifying conversion efficiency using bottles
- Big cal gas flows required
- Can not run from common manifold
- Losses due to conditioning
- Must be VERY, VERY patient

# Conditioning with 500 ppb $NO_2$

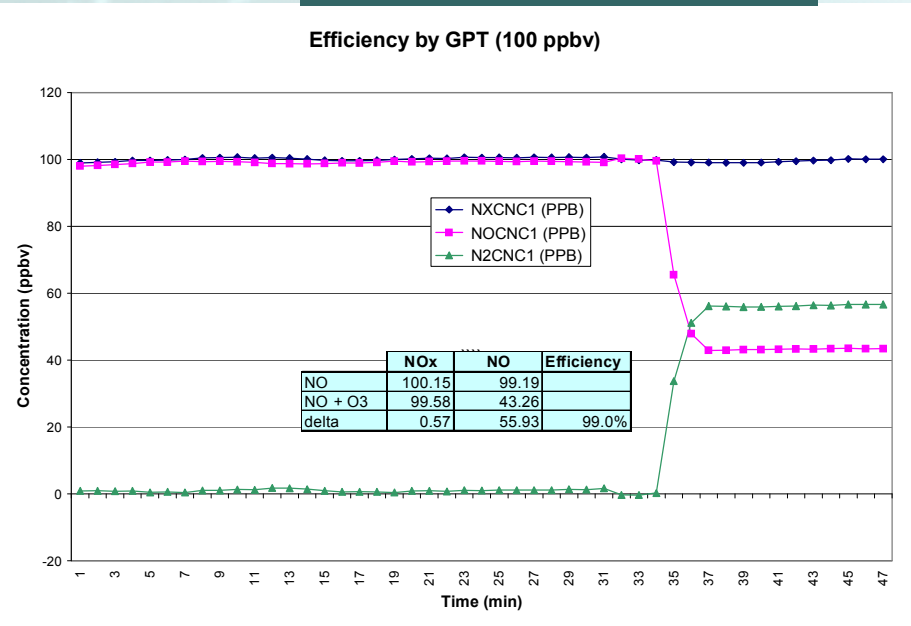


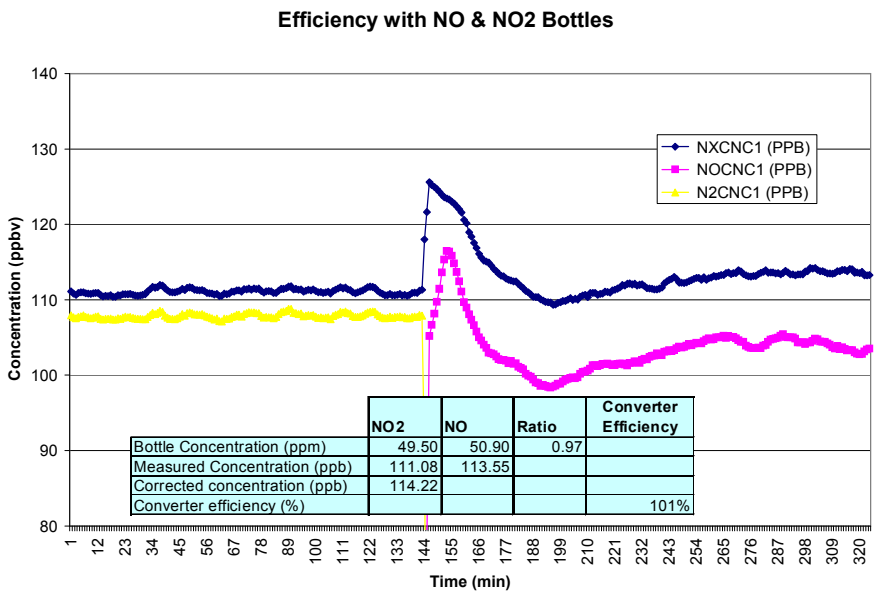
# Checking Converter Efficiency

- Gas Phase Titration (GPT) golden standard
  - Auto-referencing - independent of NO or Ozone concentration
  - Independent of MFC calibrations and matching
- $NO/NO_2$, nPan or i-Pan bottles
  - Limited by accuracy of bottles
  - Limited by accuracy and linearity of MFCs
  - Best to maintain MFC flows use ratio of bottles
  - Check for contaminants in NO and other bottle

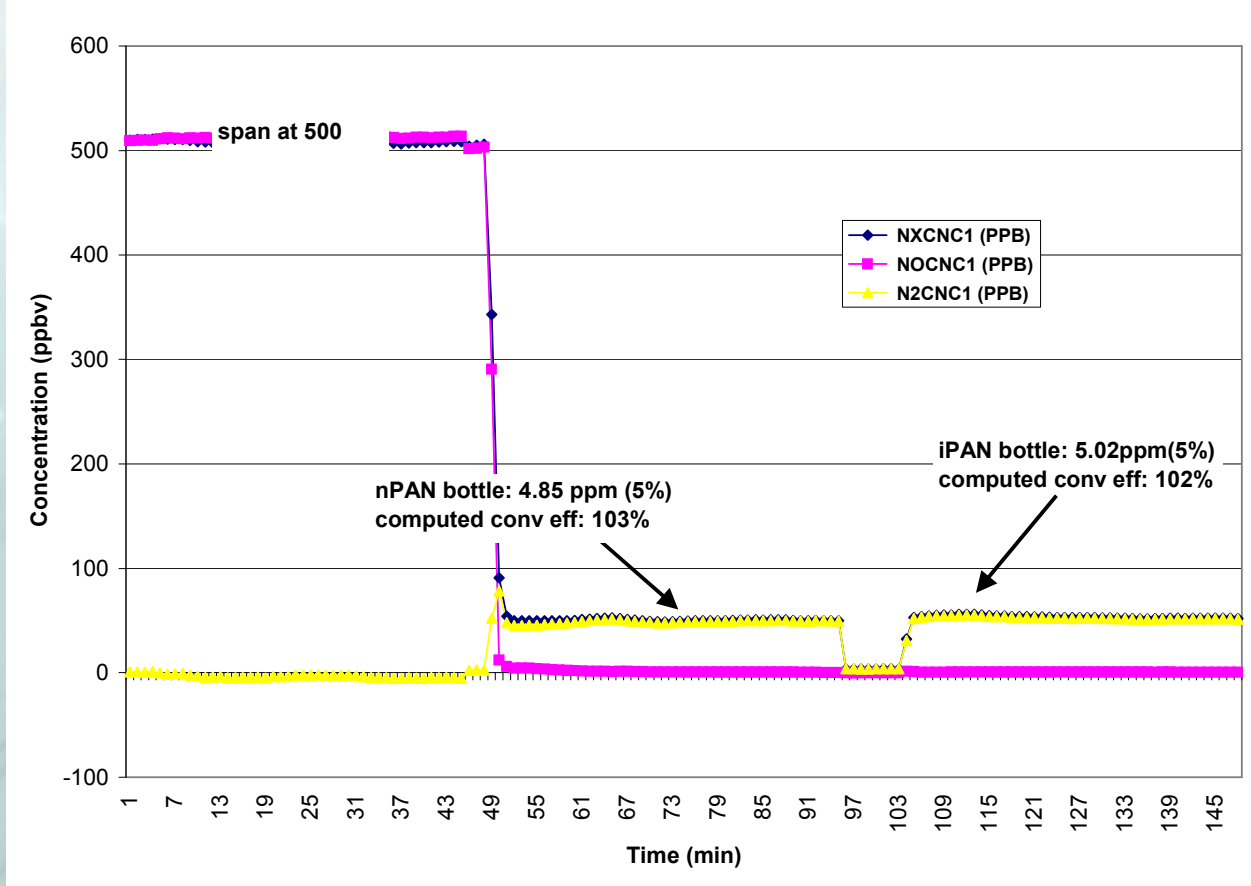
# GPT vs. NO/NO2 gas Efficiency

| Method | Efficiency |
|---|---|
| GPT | 99% |
| Gas Bottles | 101% |



# iPan/nPan Efficiency



# Interferences

- Water: no effect at zero, ~ 3% quench at span
- $NH_3$: 1 – 5 %
- Ammines ??
- Hydrocarbons

*** WATER INTERFERENCE DATA - TABLE 14**

| DATA | TEST 1 | TEST 2 | TEST 3 | TEST 4 | TEST 5 | TEST 6 | TEST 7 |
|---|---|---|---|---|---|---|---|
| R4 | 104.9 ppb | 104.3 ppb | 104.1 ppb | 106.2 ppb | 106.4 ppb | 106.1 ppb | 99.4 ppb |
| R14 | 99.1 | 98.7 | 99.0 | 100.7 | 101.2 | 100.6 | 95.1 |
| R14' | 101.3 | 100.9 | 101.2 | 102.9 | 103.4 | 102.8 | 97.2 |
| IE | -3.6 | -3.4 | -2.9 | -3.3 | -2.7 | -3.3 | -2.2 |

# Siting

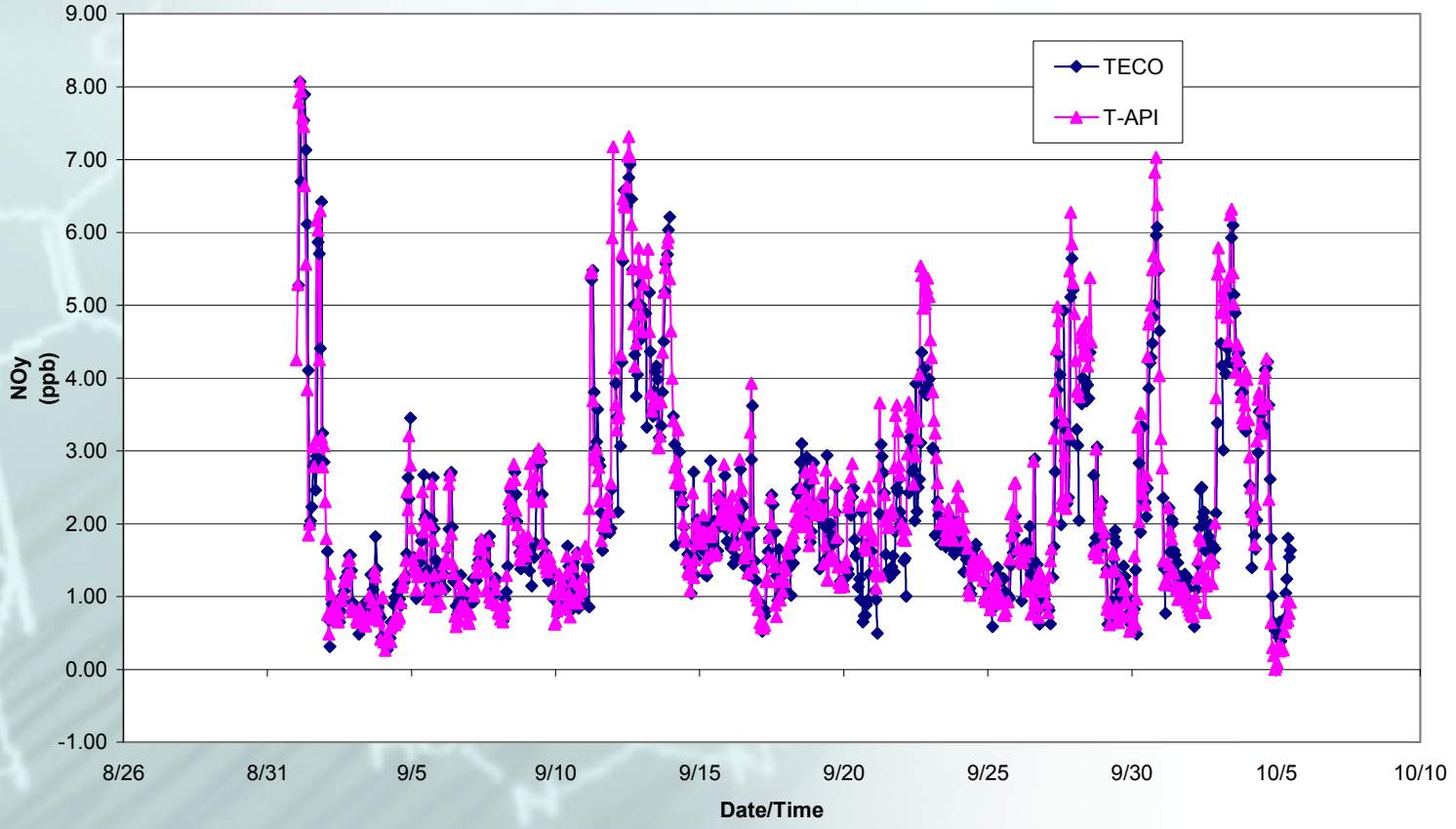
- Be aware of nearby sources of:
  - Hydrocarbons – roofing materials
  - Ammonia – sewer vents

NSF UV Spectroradiometer – Barrow, AK
Courtesy of Biospherical Instruments

Pinnacle State Park, NY

# Pinnacle State Park NOy Comparison

**Courtesy of Atmospheric Sciences Research Center**
**University at Albany - State University of NY**

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# Acknowledgements & Bibliography


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  Dennis R. Fitz, University of California, Riverside, College of Engineering, Center for Environmental Research and Technology
- Review of M200AU: NOY Converter Design Theory and Practice
  Martin Buhr, Regional Air Quality Council, Denver, CO, 1997
- AMS *Glossary of Meteorology*
  American Meteorological Society
  http://amsglossary.allenpress.com/glossary/acknowledge